(19)日本国特許庁（JP）　(12)公開特許公報（A）　(11)特許出願公開番号
特開平11－263916
(43)公開日　平成11年(1999)9月28日

(51)Int.Cl.⁶	識別記号	FI
C08L 101/00		C08L 101/00
C08K 9/04		C08K 9/04
C08L 79/04		C08L 79/04
83/00		83/00
H01L 21/314		H01L 21/314 A

審査請求　未請求　請求項の数6　OL　（全5頁）　最終頁に続く

(21)出願番号　特願平10－67287
(22)出願日　平成10年(1998)3月17日

(71)出願人　000005223
富士通株式会社
神奈川県川崎市中原区上小田中4丁目1番1号
(72)発明者　根津　東
神奈川県川崎市中原区上小田中4丁目1番1号　富士通株式会社内
(72)発明者　早野　智明
神奈川県川崎市中原区上小田中4丁目1番1号　富士通株式会社内
(74)代理人　弁理士　石田　敬　（外3名）

最終頁に続く

(54)【発明の名称】　低誘電率の回路配線用絶縁材料及びこれを用いた電子部品

(57)【要約】
【課題】　伝送遅延が減少して高速処理を可能にする電子部品における低誘電率の多層回路基板の層間絶縁膜に有用な材料を提供する。
【解決手段】　本発明の回路配線用絶縁材料は、絶縁性樹脂基剤と、フラーレンあるいはカーボンナノチューブに化学修飾を施して相溶性を向上させた化合物とを含む。

1

【特許請求の範囲】

【請求項1】 絶縁性樹脂基剤とフラーレンあるいはカーボンナノチューブに化学修飾を施した化合物とを含むことを特徴とする回路配線用絶縁材料。

【請求項2】 前記フラーレンあるいはカーボンナノチューブの炭素－炭素間の距離が4オングストローム（0．4nm）以上である．請求項1記載の回路配線用絶縁材料。

【請求項3】 前記化学修飾がシリコーン系官能基、酸素を含む置換基．不飽和結合を持つ置換基又はフッ素原子でなされている、請求項1又は2記載の回路配線用絶縁材料。

【請求項4】 前記絶縁性樹脂基剤がポリイミド又はシリコーン樹脂である、請求項1から3までのいずれか一つに記載の回路配線用絶縁材料。

【請求項5】 請求項1から4までのいずれか一つに記載の材料を硬化させて形成されていることを特徴とする回路配線用絶縁膜。

【請求項6】 請求項5記載の絶縁膜を使用した多層回路配線基板を含む電子部品。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は．半導体素子など電子デバイスを高密度に実装し、信号の高速伝搬に適した．低誘電率多層回路配線の層間絶縁材料と、このような多層回路配線基板を含む大規模集積回路（ＬＳＩ）等の電子部品に関する。

【0002】パーソナルコンピュータからハイパフォーマンスコンピュータに至るまでの各種コンピュータで使用される半導体素子の高速化は著しく．相対的に基板配線部における伝送遅延が．コンピュータの演算速度を左右するようになってきている。この結果．コンピュータの中央処理装置（ＣＰＵ）用回路基板には、樹脂薄膜を層間絶縁膜とする、高密度かつ微細な多層配線に適した樹脂薄膜配線が適用されるようになってきた。将来のより高速なコンピュータを実現するには．高密度かつ微細な多層配線を活かし、かつ信号の高速伝搬に適した低誘電率絶縁材料の開発が不可欠である。

【0003】

【従来の技術】従来、高速コンピュータに使用されている高密度実装基板材料には．エポキシ．ポリイミドなどの樹脂が使用されている。更に、最近では、より低い誘電率を有する樹脂としてオレフィン系やフッ素系の材料が注目されている。

【0004】材料の比誘電率ε_sは．クラウジウスーモソッティの式によると以下のように表される。

【0005】

【数1】

(2)

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{N\alpha}{3\varepsilon_0}$$

【0006】ただし、この式のαは材料分子の分極率、Nは単位体積あたりの分子数、ε_0は真空の誘電率である。

【0007】上式で、ε_sについて解き、α又はNで偏微分すればわかるように．分極率αが小さいほど．また単位体積中の分子数Nが小さいほど．比誘電率ε_sが小さくなる。この関係は，図1に示した$N\alpha$と比誘電率ε_sとの関係の一例を示すグラフから明らかである。以下．比誘電率のことを単に「誘電率」と称することにする。

【0008】上述のようにオレフィン系あるいはフッ素系の樹脂を用いることは．材料の分極率αを低く抑えるのに効果がある．しかし．これらの誘電率は2を下回らないことが知られている。また、これらの樹脂材料は，自己融着性や導体金属との密着性、層間のビア孔加工性など．現状では解決すべきことが多く残されている。

【0009】一方、単位体積当たりの分子数Nを小さくすることにより誘電率を下げる方法もある。例えば、単位体積当たりの分子数の少ないものとして発泡させた材料が存在するが．これらが微細配線の数μmあるいは数十μmオーダーの厚みの絶縁体として適さないことは明白である。

【0010】また、絶縁膜の軽量．低熱膨張率化を目的として、樹脂材料にガラス繊維や炭素繊維を混入して複合化することも考えられるが．ガラス繊維には誘電率を引き上げるという欠点があり、炭素繊維には絶縁耐圧を低下させるという欠点がある。

【0011】更に、分子レベルでの空間を取り入れることで材料の誘電率を低下させるために．分子内に空間のある構造を持つフラーレンなどを樹脂材料に混合する方法も考えられるが、フラーレンは限られた溶媒に．微量しか溶解せず．そのため樹脂に混合しても相分離しやすいという問題があった。

【0012】

【発明が解決しようとする課題】体誘電率の層間絶縁膜材料として将来より注目されているオレフィン系やフッ素系樹脂材料の誘電率は．2．1から2．8程度の範囲である。これまでも、これらの材料の誘電率を更に下回る材料がいくつか提案されてはいるが．現実の製造あるいは実装プロセスに対応できる特性を有し、また自己融着性や導体金属との密着性．層間のビア孔加工性など、絶縁材料として必須な性質を兼ね備えた、実用的な低誘電率層間絶縁材料に対して依然として大きな期待が寄せられている。

【0013】本発明は、それに応えて．微細パターンの回路配線用の低誘電率の絶縁材料として有用な新しい材料を提供するのを目的とする。また．このような新しい

低誘電率絶縁材料から形成した絶縁膜を含む電子部品を提供することも本発明の目的である。

【0014】

【課題を解決するための手段】本発明の回路配線用絶縁材料は、絶縁性樹脂基剤とフラーレンあるいはカーボンナノチューブに化学修飾を施した化合物とを含むことを特徴とする。

【0015】このように、本発明は、絶縁膜材料の基剤として用いられる樹脂との相溶性が本質的によくないフラーレンやカーボンナノチューブに化学修飾を施すことによって樹脂との相溶性を高めることで、樹脂中へのフラーレンやカーボンナノチューブの分散量を大きくし、形成した絶縁膜の低誘電率化を達成したものである。

【0016】フラーレンやカーボンナノチューブは、炭素原子のみから構成された分子内に空間を持つ構造の物質としてよく知られている。フラーレンは、表面に炭素原子から形成された網目構造のある中空の球状分子の化合物であり、カーボンナノチューブは同様に表面に炭素原子から形成された網目構造のある、中空の円筒状分子の化合物である。これらは、合成してもよく、あるいは市販のものを使用してもよい。

【0017】フラーレンなどは、例えば、有機リチウムやグリニャール試薬を用いることにより化学修飾を施すことができる（永島、神野、伊藤、日本化学会誌、Vol. 2、p91（1997）を参照）。これにより、フラーレンなどとポリイミドなどの絶縁樹脂との相溶性を向上させ、樹脂中の空間を大きくすることにより、形成した絶縁膜の誘電率を低下させることができる。あるいは、化学修飾によりフラーレンなどに絶縁樹脂との反応性を付与することもできる。

【0018】フラーレンあるいはカーボンナノチューブの化学修飾は、例えばシリコーン系官能基や酸素を含む置換基などで施すことができる。シリコーン系官能基や酸素を含む置換基の例は、$-Si(CH_3)_3$、$-Si(CH_3)_2OCH_3$、$-Si(CH_3)(OCH_3)_2$、$-Si(CH_3)(OCH(CH_3)_2)_2$等であり、これらで化学修飾されたフラーレンあるいはカーボンナノチューブは絶縁材料の基剤樹脂との相溶性が向上する。不飽和結合を持つ官能基を加えて、フラーレンあるいはカーボンナノチューブの反応性を増加させてもよい。不飽和結合を持つ官能基の代表例は、アリル基、アリール基、$-C\equiv C-R$（Rはアルキル基）等である。また、フラーレンあるいはカーボンナノチューブ分子に水素や、ふっ素を付加させて、これらの分子の共役系の一部を飽和結合にすることも、絶縁材料の誘電率を低下させるために効果がある。

【0019】絶縁材料の誘電率の低下に寄与する空間を形成するためには、フラーレン等の分子長軸方向の炭素－炭素間の距離が少なくとも4オングストローム（0.4nm）以上あることが好ましい。例として、分子長軸方向の炭素－炭素間の距離が4オングストローム（0.4nm）以上のフラーレンとしては、C_{20}、C_{24}、C_{26}、C_{28}、C_{30}、C_{32}、C_{34}、C_{36}、C_{60}、C_{70}、C_{76}、C_{78}、C_{80}、C_{100}、C_{240}、C_{320}、C_{540}などが考えられる。

【0020】本発明の絶縁材料は、化学修飾したフラーレンあるいはカーボンナノチューブを、絶縁材料の基剤樹脂と混合して調製することができる。必要に応じ、溶媒を使用しても差し支えない。フラーレンあるいはカーボンナノチューブは、基剤樹脂又は基剤樹脂溶液に対する溶解度に依存するとは言え、基剤樹脂又は基剤樹脂溶液に飽和するまで加えることができる。この最大限の添加量を用いた場合に、例えば形成した絶縁膜の耐熱性等が問題となる場合には、フラーレン等の添加量を減少させるべきである。いずれにせよ、本発明の絶縁材料に混入するフラーレンあるいはカーボンナノチューブの量は、基剤樹脂の種類や絶縁膜に要求される特性に応じて実験により簡単に決定することができる。

【0021】基剤樹脂は、多層配線の製造に用いられる低誘電率の樹脂のいずれでもよい。基剤樹脂がポリイミドあるいはシリコーン樹脂であると、これらは特に耐熱性にも優れることから、電子部品の組み立て工程や製品の信頼性の面で有利である。

【0022】本発明の絶縁材料から多層回路基板の層間絶縁膜を形成するには、絶縁材料を基板に塗布し、乾燥後、基剤樹脂を硬化させればよく、これは多層回路基板の分野でよく知られた手法であり、ここで詳しく説明するには及ばない。

【0023】本発明の絶縁材料から形成した絶縁膜は、基剤樹脂に分散した、分子レベルでの空間を備えた炭素化合物の効果により、低誘電率、低熱膨張、高絶縁性を具備する。この絶縁膜を層間絶縁膜として用いた、例えばLSI等の電子部品は、高密度かつ微細な多層配線構造を備えることができ、各種コンピュータの演算速度の向上に大きく貢献する。

【0024】

【実施例】次に、本発明の実施例を説明するが、言うまでもなく本発明はこれらの実施例に限定されるものではない。

【0025】〔実施例1〕C_{60}フラーレン（アルドリッチ社製）を70gのテトラヒドロフラン（THF）に過飽和になるまで溶解後、グリニャール試薬$ClMgCH_2SiMe_2(OCH(Me)_2)$（この式のMeはメチル基を表す）を用いて、20℃の温度で2時間の付加反応を行った。付加反応後、溶媒のTHFを除去してから、この化学修飾したC_{60}フラーレンを、特開平8-259784号公報で示されるように、6-メチル-1,4,5,8-ジメタノ-1,2,3,4,4a,5,8,8a-オクタヒドロナフタレンを公知の方法で開環重合し、水素添加して得た脂環式ポリオレフィンの10

重量%THF溶液に加えて、化学修飾C_{60}フラーレンで飽和させた絶縁材料溶液を作った。

【0026】次に、この溶液をシリコン基板上にスピンコートし、乾燥後、220℃で5分の条件で熱硬化させた。更に、アフターキュアとして、酸素濃度10ppm以下の窒素雰囲気中にて200℃で5時間の熱硬化を行い、絶縁膜を形成した。この絶縁膜の誘電率を、金電極（1mm×1mm）を蒸着し1MHzで測定したところ、2.2であった。

【0027】〔実施例2〕C_{60}フラーレン（アルドリッチ社製）を70gのテトラヒドロフラン（THF）に過飽和になるまで溶解後、グリニャール試薬ClMgCH$_2$SiMe$_2$（OCH(Me)$_2$）（この式のMeはメチル基を表す）を用いて、20℃の温度で2時間の付加反応を行った。この生成物に対し、更にt-ブチルリチウムにより付加反応（20℃、2時間）を行って、C_{60}フラーレンに水素とt-ブチル基を付加させた。反応終了後、溶媒のTHFを除去してから、この化学修飾したC_{60}フラーレンを実施例1で使用したのと同じ脂環式ポリオレフィンの10重量%THF溶液に加えて、化学修飾C_{60}フラーレンで飽和させた絶縁材料溶液を作った。

【0028】次に、この溶液をシリコン基板上に塗布し、乾燥後、220℃で5分の条件で熱硬化させた。更に、アフターキュアとして、酸素濃度10ppm以下の＊窒素雰囲気中にて200℃で5時間の熱硬化を行い、絶縁膜を形成した。この絶縁膜の誘電率を実施例1で説明したとおりに測定したところ、誘電率は2.0であった。

【0029】〔比較例〕実施例1、2で使用したのと同じC_{60}フラーレンを、やはり実施例1、2で使用したのと同じ脂環式ポリオレフィンの10重量%THF溶液に飽和するまで溶解させた。こうして調製した絶縁材料の溶液を基板上に塗布、乾燥し、220℃、5分の条件で熱硬化させた。更に、アフターキュアとして、酸素濃度10ppm以下の窒素雰囲気中にて200℃、5時間の熱硬化を行い、絶縁膜を形成した。実施例1で説明した方法で測定したこの絶縁膜の誘電率は2.8であった。

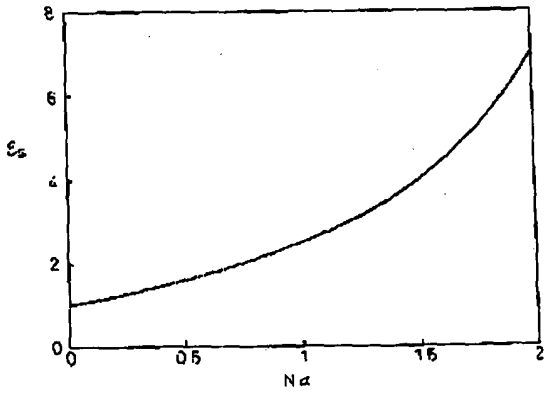
【0030】

【発明の効果】以上説明したように、本発明によれば、分子レベルで空間を形成できるフラーレンやカーボンナノチューブを絶縁材料中に効果的に取り込むことができるため、微細パターンに適用できる低誘電率の絶縁膜を提供すること、及びこの絶縁膜を含み高速の信号伝播に適した多層回路基板を含む電子部品を提供することが可能になる。

【図面の簡単な説明】

【図1】材料の単位体積中の分子数N及び分極率αの積と、比誘電率εsとの関係を示すグラフである。

【図1】



フロントページの続き

(51)Int.Cl.°	識別記号	FI	
H01L 21/768		H01L 21/90	S

(72)発明者 佐藤 博之
神奈川県川崎市中原区上小田中4丁目1番1号 富士通株式会社内
(72)発明者 横内 貴志男
神奈川県川崎市中原区上小田中4丁目1番1号 富士通株式会社内
(72)発明者 福山 俊一
神奈川県川崎市中原区上小田中4丁目1番1号 富士通株式会社内
(72)発明者 中田 義弘
神奈川県川崎市中原区上小田中4丁目1番1号 富士通株式会社内

* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The insulating material for circuit wiring characterized by including the compound which gave chemical modification in an insulating resin matrix, fullerene, or a carbon nanotube.
[Claim 2] The insulating material for circuit wiring according to claim 1 whose distance between the aforementioned fullerene or the carbon-carbon of a carbon nanotube is more than 4A (0.4nm).
[Claim 3] The insulating material for circuit wiring according to claim 1 or 2 by which the aforementioned chemical modification is made by the silicone system functional group, the substituent containing oxygen, the substituent with a unsaturated bond, or the fluorine atom.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention mounts electron devices, such as a semiconductor device, with high density, and relates to electronic parts, such as layer insulation material of the low dielectric constant multilayer circuit wiring suitable for high-speed propagation of a signal, and a large-scale integrated circuit (LSI) containing such a multilayer circuit wiring substrate.
[0002] Improvement in the speed of the semiconductor device used by various computers until it results [from a personal computer] in a high performance computer is remarkable, and the transit delay in the substrate wiring section influences the operation speed of a computer increasingly relatively. Consequently, the resin thin film wiring suitable for the high-density and detailed multilayer interconnection which uses a resin thin film as a layer insulation film has come to be applied to the circuit board for central processing units (CPU) of a computer. In order to realize a future more nearly high-speed computer, development of the low dielectric constant insulating material which was suitable for high-speed propagation of a signal taking advantage of the high-density and detailed multilayer interconnection is indispensable.
[0003]
[Description of the Prior Art] Conventionally, resins, such as epoxy and a polyimide, are used for the high-density-assembly substrate material currently used for the high-speed computer. Furthermore, recently, the material of an olefin system or a fluorine system attracts attention as a resin which has a low dielectric constant more.
[0004] Specific-inductive-capacity epsilons of material According to the formula of Clausius-MOSOTTEI, it is expressed as follows.
[0005]
[Equation 1]

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{N\alpha}{3\varepsilon_0}$$

[0006] However, alpha of this formula is the polarizability of a material molecule, and N is the molecularity per unit volume, and epsilon 0. It is the dielectric constant of vacuum.
[0007] an upper formula -- epsilons ******** -- if it solves and a partial differential is carried out by alpha or N, so that it may understand and the molecularity N in a unit volume is so small that polarizability alpha is small -- specific-inductive-capacity epsilons It becomes small. This relation is Nalpha and specific-inductive-capacity epsilons which were shown in drawing 1 . It is clear from the graph which shows an example of a relation. Hereafter, the thing of specific inductive capacity will only be called a "dielectric constant."
[0008] Using the resin of an olefin system or a fluorine system as mentioned above has an effect in stopping the polarizability alpha of material low. However, it is known that these dielectric constants will not be less than 2. moreover, such resin material -- a self welding property and a conductor -- adhesion with a metal, and the beer between layers -- a hole -- many things which should be solved are left behind in the present condition, such as processability

[0009] There is also the method of on the other hand lowering a dielectric constant by making molecularity N per unit volume small. For example, although the material made to foam as what has the few molecularity per unit volume exists, it is clear that these are not suitable as an insulator of the thickness of several micrometers or dozens of micrometer order of detailed wiring.
[0010] Moreover, although mixing and composite-izing a glass fiber and a carbon fiber into resin material for the purpose of lightweight [of an insulator layer] and the formation of a low-fever expansion coefficient is also considered, a glass fiber has the fault of pulling up a dielectric constant, and a carbon fiber has the fault of reducing isolation voltage.
[0011] Furthermore, although how to mix the fullerene which has structure with space in a molecule into resin material was also considered in order to reduce the dielectric constant of material by taking in the space in molecule level, fullerene had a title, while calling it the phase separation plain-gauze cone, even if it dissolved only the minute amount in the limited solvent, therefore mixed to the resin.
[0012]
[Problem(s) to be Solved by the Invention] The dielectric constant of the olefin system which attracts attention from the future as a layer insulation film material of a body dielectric constant, or fluorine system resin material is about 2.1 to 2.8 range. the property that it can respond to actual manufacture or a mounting process although some material which is further less than the dielectric constant of such material is proposed until now -- having -- moreover, a self welding property and a conductor -- adhesion with a metal, and the beer between layers -- a hole -- it has a still great hope to a practical low dielectric constant layer insulation material which has a property indispensable as insulating materials, such as processability
[0013] this invention aims at offering a new material useful as an insulating material of a low dielectric constant for circuit wiring of a detailed pattern in response to it. Moreover, it is also the purpose of this invention to offer the electronic parts containing the insulator layer formed from such a new low dielectric constant insulating material.
[0014]
[Means for Solving the Problem] The insulating material for circuit wiring of this invention is characterized by including the compound which gave chemical modification in an insulating resin matrix, fullerene, or a carbon nanotube.
[0015] Thus, when compatibility with the resin used as a basis of insulator layer material essentially gives chemical modification to the fullerene and the carbon nanotube which are not good, this invention is raising compatibility with a resin, and attains low dielectric constant-ization of the insulator layer which enlarged fullerene to the inside of a resin, and variance of a carbon nanotube, and formed them.
[0016] Fullerene and the carbon nanotube are well known as matter of the structure which has space in the molecule which consisted of only carbon atoms. Fullerene is the compound of the globular molecule of hollow with the network structure formed in the front face from the carbon atom, and a carbon nanotube is the compound of a cylinder-like molecule in the air with the network structure similarly formed in the front face from the carbon atom. These may be compounded or may use a commercial thing.
[0017] Fullerene etc. can give chemical modification by using for example, an organic lithium and a Grignard reagent (see Nagashima, Jinno, Ito, the Chemical Society of Japan, Vol.2, and p91 (1997)). The dielectric constant of the formed insulator layer can be reduced by raising the compatibility of fullerene etc. and insulating resins, such as a polyimide, and enlarging space in a resin by this. Or chemical modification can also give reactivity with an insulating resin to fullerene etc.
[0018] Chemical modification of fullerene or a carbon nanotube can be given by the substituent containing for example, a silicone system functional group or oxygen etc. the example of the substituent containing a silicone system functional group or oxygen -Si (CH3)3, -Si(CH3)2 OCH3, -Si (CH3) (OCH3)2, and -Si (CH3) (OCH2 (CH3))2 etc. -- it is -- compatibility of the carbon nanotube [the fullerene or the carbon nanotube] by which chemical modification was carried out by these with the basis resin of an insulating material improves A functional group with a unsaturated bond may be added and the reactivity of fullerene or a carbon nanotube may be made to increase. The examples of representation of a functional group with a unsaturated bond are an allyl group, an aryl group, -C**C-R (R is an alkyl group), etc. Moreover, hydrogen and fluorine are made to add to

fullerene or a carbon nanotube molecule, and in order that making saturation combination a part of conjugated system of these molecules may also reduce the dielectric constant of an insulating material, it is effective.

[0019] In order to form the space which contributes to decline in the dielectric constant of an insulating material, a certain thing has a desirable distance between the carbon 1 carbon of the directions of a molecule major axis, such as fullerene, more than at least 4A (0.4nm). as an example -- the distance between the carbon 1 carbon of the direction of a molecule major axis -- as the fullerene more than 4A (0.4nm) -- C20, C24, C26, C28, C30, C32, C36, C50, C60, C70, C76, C78, C80, C180, C240, C320, and C540 etc. -- it thinks

[0020] The insulating material of this invention can be mixed with the basis resin of an insulating material, and can prepare FURENEN or the carbon nanotube which carried out chemical modification. If needed, even if it uses a solvent, it does not interfere. FURENEN or a carbon nanotube can be added until it is saturated in a basis resin or a basis resin solution, although it is dependent on the solubility to a basis resin or a basis resin solution. You should decrease additions, such as fullerene, when the thermal resistance of the insulator layer formed when this maximum addition was used etc. poses a problem. Anyway, according to the property required of the kind and insulator layer of a basis resin, an experiment can determine easily the amount of the fullerene mixed in the insulating material of this invention, or a carbon nanotube.

[0021] Any of the resin of a low dielectric constant used for manufacture of a multilayer interconnection are sufficient as a basis resin. Since especially these are excellent also in thermal resistance in a basis resin being a polyimide or silicone resin, it is advantageous in respect of the reliability of the assembler of electronic parts degree, or a product.

[0022] In order to form the layer insulation film of a multilayered circuit board from the insulating material of this invention, this is the technique which the field of a multilayered circuit board is sufficient as, and was known, and it is not necessary to explain it in detail here that what is necessary is to apply an insulating material to a substrate and just to stiffen a basis resin after dryness.

[0023] The insulator layer formed from the insulating material of this invention possesses a low dielectric constant, low-fever expansion, and high insulation according to the effect of the carbon compound equipped with the space in molecule level distributed to the basis resin. For example, it used this insulator layer as a layer insulation film, electronic parts, such as LSI, can be equipped with high-density and detailed multilayer-interconnection structure, and contribute to improvement in the operation speed of various computers greatly.

[0024]

[Example] Next, although the example of this invention is explained, needless to say, this invention is not limited to these examples.

[0025] [Example 1] The addition reaction of 2 hours was performed at the temperature of 20 degrees C after the dissolution using Grignard reagent ClMgCH2 SiMe2 (Me of this (OCH2 (Me)) formula expresses a methyl group) until it became supersaturation to the 70g tetrahydrofuran (THF) about C60 fullerene (Aldrich make). It is 6-methyl, as JP,8-259784,A shows this C60 fullerene that carried out chemical modification after an addition reaction, after removing THF of a solvent. - 1, 4, 5, 8-dimethano - The insulating material solution which was saturated with chemical modification C60 fullerene in addition to the 10-% of the weight THF solution of the alicyclic polyolefine which carried out ring opening polymerization of the 1, 2, 3, 4,a [4], 5, 8, and 8a-octahydronaphthalene, hydrogenated it, and obtained it by the well-known method was made

[0026] Next, the spin coat of this solution was carried out on the silicon substrate, and it was made to heat-harden on the conditions for 5 minutes by 220 degrees C after dryness. Furthermore, as after-cure, heat curing of 5 hours was performed at 200 degrees C in the nitrogen-gas-atmosphere mind of 10 ppm or less of oxygen densities, and the insulator layer was formed. It was 2.2, when the vacuum evaporationo of the golden electrode (1mmx1mm) was carried out and the dielectric constant of this insulator layer was measured by 1MHz.

[0027] [Example 2] The addition reaction of 2 hours was performed at the temperature of 20 degrees C after the dissolution using Grignard reagent ClMgCH2 SiMe2 (Me of this (OCH2 (Me)) formula expresses a methyl group) until it became supersaturation to the 70g tetrahydrofuran (THF) about C60 fullerene (Aldrich make). t-butyl lithium performed the addition reaction (20 degrees C, 2

hours) further, and hydrogen and t-butyl were made to add to C60 fullerene to this product. After the reaction end, after removing THF of a solvent, the insulating material solution which saturated with chemical modification C60 fullerene this C60 fullerene that carried out chemical modification in addition to the 10-% of the weight THF solution of the same alicyclic polyolefine as having used it in the example 1 was made.

[0028] Next, this solution was applied on the silicon substrate and it was made to heat-harden on the conditions for 5 minutes by 220 degrees C after dryness. Furthermore, as after-cure, heat curing of 5 hours was performed at 200 degrees C in the nitrogen-gas-atmosphere mind of 10 ppm or less of oxygen densities, and the insulator layer was formed. The dielectric constant was 2.0 when it measured as the example 1 explained the dielectric constant of this insulator layer.

[0029] [Example of comparison] The C60 same fullerene as having used it in the examples 1 and 2 was dissolved until it was saturated in the 10-% of the weight THF solution of the same alicyclic polyolefine as having used it in the examples 1 and 2 too. In this way, the prepared solution of an insulating material was applied on the substrate, and it dried, and was made to heat-harden on 220 degrees C and the conditions for 5 minutes. Furthermore, as after-cure, 200 degrees C and heat curing of 5 hours were performed in the nitrogen-gas-atmosphere mind of 10 ppm or less of oxygen densities, and the insulator layer was formed. The dielectric constant of this insulator layer measured by the method explained in the example 1 was 2.8.

[0030]

[Effect of the Invention] Since the fullerene and the carbon nanotube which can form space on molecule level can be incorporated effectively in an insulating material according to this invention as explained above, it becomes possible to offer the insulator layer of a low dielectric constant applicable to a detailed pattern, and to offer the electronic parts containing the multilayered circuit board which was suitable for high-speed signal propagation including this insulator layer.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Conventionally, resins, such as epoxy and a polyimide, are used for the high-density-assembly substrate material currently used for the high-speed computer. Furthermore, recently, the material of an olefin system or a fluorine system attracts attention as a resin which has a low dielectric constant more.
[0004] Specific-inductive-capacity epsilons of material According to the formula of Clausius-MOSOTTEI, it is expressed as follows.
[0005]
[Equation 1]

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} = \frac{N\alpha}{3\varepsilon_0}$$

[0006] However, alpha of this formula is the polarizability of a material molecule, and N is the molecularity per unit volume, and epsilon 0. It is the dielectric constant of vacuum.
[0007] an upper formula -- epsilons ******** -- if it solves and a partial differential is carried out by alpha or N, so that it may understand and the molecularity N in a unit volume is so small that polarizability alpha is small -- specific-inductive-capacity epsilons It becomes small. This relation is Nalpha and specific-inductive-capacity epsilons which were shown in drawing 1 . It is clear from the graph which shows an example of a relation. Hereafter, the thing of specific inductive capacity will only be called a "dielectric constant."
[0008] Using the resin of an olefin system or a fluorine system as mentioned above has an effect in stopping the polarizability alpha of material low. However, it is known that these dielectric constants will not be less than 2. moreover, such resin material -- a self welding property and a conductor -- adhesion with a metal, and the beer between layers -- a hole -- many things which should be solved are left behind in the present condition, such as processability
[0009] There is also the method of on the other hand lowering a dielectric constant by making molecularity N per unit volume small. For example, although the material made to foam as what has the few molecularity per unit volume exists, it is clear that these are not suitable as an insulator of the thickness of several micrometers or dozens of micrometer order of detailed wiring.
[0010] Moreover, although mixing and composite-izing a glass fiber and a carbon fiber into resin material for the purpose of lightweight [of an insulator layer] and the formation of a low-fever expansion coefficient is also considered, a glass fiber has the fault of pulling up a dielectric constant, and a carbon fiber has the fault of reducing isolation voltage.
[0011] Furthermore, although how to mix the fullerene which has structure with space in a molecule into resin material was also considered in order to reduce the dielectric constant of material by taking in the space in molecule level, fullerene had a title, while calling it the phase separation plain-gauze cone, even if it dissolved only the minute amount in the limited solvent, therefore mixed to the resin.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The molecularity N in the unit volume of material and the product of polarizability alpha, and specific-inductive-capacity epsilons It is the graph which shows a relation.

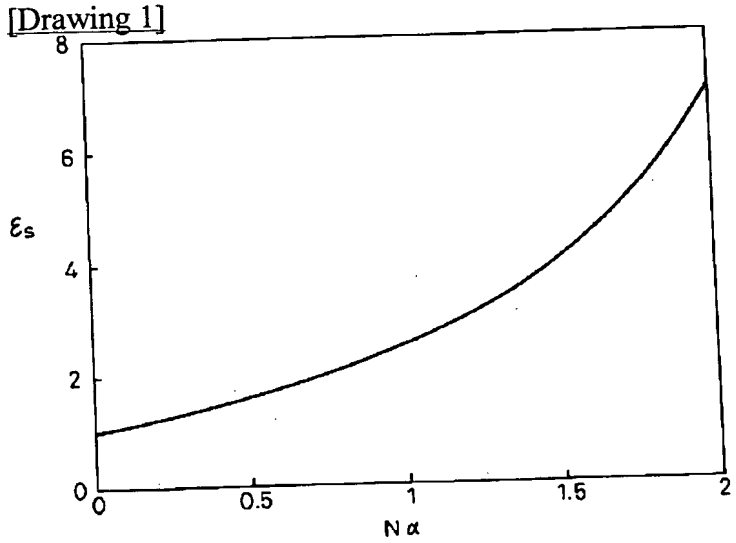
[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-263916
(43)Date of publication of application : 28.09.1999

(51)Int.Cl. C08L101/00
C08K 9/04
C08L 79/04
C08L 83/00
H01L 21/314
H01L 21/768

(21)Application number : 10-067287
(22)Date of filing : 17.03.1998

(71)Applicant : FUJITSU LTD
(72)Inventor : MATSUURA AZUMA
HAYANO TOMOAKI
SATO HIROYUKI
YOKOUCHI KISHIO
FUKUYAMA SHUNICHI
NAKADA YOSHIHIRO

(54) LOW DIELECTRIC CONSTANT INSULATING MATERIAL FOR WIRING CIRCUIT AND ELECTRONIC PARTS USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a low dielectric constant insulating material for wiring circuit of fine patterns by including an insulating resin base and compounds which us obtained from chemical modification of a fullerence or a carbon nano- tube.
SOLUTION: This material comprises (A) an insulating resin base (polyimide, silicone resin and the like) and (B) the compounds obtained by chemically modifying the fullerene (hollow spheroidal molecular compounds having carbon network structure on the surface) or the carbon nano-tube (hollow cylindrical molecular compounds having carbon network structure on the surface), with compounds including silicone based functional groups, or substituents including oxygen [-Si(CH3)3 or -Si(CH3)2OCH3 or the like]. For forming space contributing to the reduction of the dielectric constant of the insulating material, the fullerenes or the like, preferably have angstrom or more of carbon-carbon distance of the molecular longitudinal axis of the fullerenes (C20 or C30 fullerene or the like).

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]